GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

PROJECT INITIATION

Date: 2/10/71

Project Title: Tracer Sensitive Tapes

Project No.: A-1308

Project Director: Mr. W. H. Burrows

Sponsor: National Aeronautics and Space Administration

Effective February 2, 1971 Estimated to run until: December 1, 1971

Type Agreement: Contract No. NAS8-26759 Amount: $24,999.00

Reports: Monthly Progress Reports
Final Report

Contact Person: Administrative
Mr. R. J. Whitcomb, GTR RR
276 Engineering Experiment Station
Campus

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GEORGIA INSTITUTE OF TECHNOLOGY
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PROJECT TERMINATION

Date 3/9/72

PROJECT TITLE: Tracer Sensitive Tapes

PROJECT NO: A-1308

PROJECT DIRECTOR: Mr. W. H. Burrows

SPONSOR: NASA - MSFC

TERMINATION EFFECTIVE: 12/31/71

CHARGES SHOULD CLEAR ACCOUNTING BY: 1/31/72

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GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

March 1, 1971

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

Attention: Mr. Frederick E. Wells

Subject: First Monthly Report, Project 1308
Tracer Sensitive Tapes

Dear Mr. Wells:

A preliminary search revealed only two candidate trace gases which were chemically active, non-toxic, and gaseous over all on a major portion of the specified temperature range. Nitrous oxide (N_2O) condenses somewhat above the minimum specified temperature, but meets the other qualifications. Gaseous oxygen appears to meet all of the project specifications. One portion of the literature search was therefore directed toward the standard test methods for the two gases.

None of the nitrous oxide methods examined to date appear to be adaptable to a tape system. Of the possible systems for detecting traces of oxygen, two appear to offer the most promise. Absorption of oxygen in alkaline ferrous tartrate followed by color development with a solution of 1,10-phenanthroline in an acetate buffer would leave a light spot where the ferrous ion had been oxidized. Alternatively, absorption into an indigo carmine solution would produce sharp color development with escaping oxygen. Reagent stability is better with the first method, while the second offers somewhat greater sensitivity. Other candidate chemical systems are known and may prove to be more suitable in laboratory testing.

The envisioned construction of the tape consists of a vapor impermeable backing and a filter paper contact pad. Between the impermeable backing and the paper are a series of capsules to be crushed in sequence to displace air from the test paper, to displace the original liquid with an absorbant, and finally (if needed) to add the color developing reagent.

A list of the references examined to date is attached.

Yours very truly,

[redacted]

W. H. Burrows, Head
Special Projects

WHB/sc

A-1308 Bibliography

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GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

March 29, 1971

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

Attention: Mr. Frederick E. Wells

Subject: Second Monthly Report, Project A-1308
Contract No. NAS8-26759 - Tracer Sensitive Tapes.

Dear Mr. Wells:

Literature Search

The literature search for candidate materials and indicator reactions has continued. In addition to the oxygen tests previously discussed, three additional trace gases appear to merit laboratory examination:

1. Nitrous oxide, which is non-toxic, non-flammable, and which liberates iodine from hydrogen iodide. The test reagent for this gas could be mildly acidified starch iodide paper, moist.

2. Carbon monoxide, 100 ppm permissible for 8 hrs, lower flammability limit in air 12.7% by volume. CO reduces yellow palladium salts to palladium black. Alternately, in the presence of a palladium catalyst, it reduces salts of molybdenum heteropolyacids,e.g., ammonium phosphomolybdate or ammonium silicomolybdate, to molybdenum blue. Test materials for CO might be:

a. Silica gel or paper impregnated with palladium chloride.

b. Silica gel impregnated with palladium chloride and ammonium molybdate.

c. Silica gel impregnated with palladium sulfate and ammonium molybdate.

d. Palladium chloride and ammonium phosphomolybdate dispersed in acetone.

3. Ethylene, non-toxic, lower flammability limit in air 3% by volume. Ethylene reduces palladium salts and heteropoly molybdates as does carbon monoxide. The color tests cited above for CO might also be applied to ethylene.

Experimental Work

Reagents for preliminary experimental work have been ordered, most have been received, and solutions for preliminary tests are being prepared. It is anticipated that the initial screening program will be well under way during April. This program is expected to include the following tests:

1. For oxygen (air):
   a. Alkaline ferrous tartrate and 1,10 phenanthroline.
   b. Indigo carmine.
2. For nitrous oxide:
   a. Moist starch iodide paper.
   b. Starch iodide paper moistened with dilute acetic acid.
3. For carbon monoxide:
   a. Silica gel impregnated with palladium chloride.
   b. Silica gel impregnated with palladium chloride and ammonium molybdate.
   c. Silica gel impregnated with palladium sulfate and ammonium molybdate.
   d. Paper impregnated with palladium chloride and ammonium molybdate then moistened with acetone.
4. For Ethylene (less than 3% in air):
   The tests outlined above for carbon monoxide.

Discussion

The tentatively suggested test mixtures and methods each have unique advantages and disadvantages. The oxygen systems are safe and sensitive but may require impracticable measures to exclude ambient air. Nitrous oxide, though safe and non-corrosive may not give a sufficiently sensitive color test. Carbon monoxide at concentrations sufficiently low to be non-toxic can be detected, but its effects on aerospace materials at elevated temperatures and pressures may be intolerable. While there are no obvious handicaps for ethylene as a trace gas, its suitability remains subject to experimental proof.

Silica gel impregnated with palladium sulfate and ammonium molybdate offers a progressive color change which can be related to the concentration of either carbon monoxide or ethylene and some tolerance for variations

of temperature and humidity. Its preparation, however, is somewhat more laborious than that of the other test systems. Silica gel treated with palladium chloride, dried, then treated with an oxidant solution such as cupric chloride or ammonium nitrate will darken on exposure to carbon monoxide and regain its color in a steam of carbon monoxide-free air. The extent to which its indefinite shelf life would be offset by reduced sensitivity is not known. The palladium chloride-ammonium phosphomolybdate-acetone system may require some ingenuity in adaptation from a test tube method to a tape substrate.

Although it is anticipated that one or more of the test systems outlined in this summary will meet the project objectives, the search for additional test systems will continue.

Respectfully submitted,

[redacted]

W. H. Burrows,
Project Director

WHB/mw

ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

April 29, 1971

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

Attention: Mr. M. C. Stellman

Subject: Third Monthly Report, Project A-1308
Contract No. NAS8-26759 - Tracer Sensitive Tapes

Introduction

Progress Report No. 2 listed several candidate systems based upon literature studies. Of these, reduction of palladium salts by carbon monoxide or ethylene has proven to be the most promising. Diborane was found to be both pyrophoric and highly toxic,* consequently, no experimental work is anticipated with this material. The reported liberation of iodine from acidulated iodides by nitrous oxide was tested by exposing starch iodide paper, moistened with dilute acetic acid, to nitrous oxide. No apparent color change occurred; conseqently, further experiments with this material have been deferred. Experiments with oxygen as tracer gas were postponed until the following report period.

Experimental

Experimental work during this period has consisted mainly of screening experiments based upon reduction of palladium salts to palladium black and reduction of yellow heteropoly molybdates to molybdenum blue in the presence of a palladium catalyst.

Support materials used for the palladium salts were (a) gas chromatography grade silica gel powder, (b) Mylar-backed TLC (thin layer chromatography) sheets, and (c) silica sheets prepared in the labora-

*Sax, N. Irving, "Dangerous Properties of Industrial Materials," 2nd ed., New York, Reinhold Publishing Corp, p. 468

tory. Impregnants consisted of dilute solutions of (a) palladium chloride in water, (b) palladium chloride in water and acetone, and (c) palladium sulfate dissolved in dilute sulfuric acid and dried.

Although all of the test specimens darkened in mixtures of carbon monoxide or ethylene, the greatest sensitivity was shown by palladium sulfate on laboratory prepared silica sheets. Contrary to the reports found in the literature, treatment of silica gel with palladium salt solutions, or with palladium salts and ammonium molybdate, did not produce a bright yellow color. Specimens so treated gave only the palladium black reaction with carbon monoxide or ethylene.

A slurry was prepared by mixing 0.5 g of ammonium-12-molybdophosphate in 10 ml of acetone, adding sufficient palladium sulfate solution to produce about 250 μg of palladium per gram of dry product, then mixing well with 5 g of silical gel, followed by air drying. Test specimens were prepared by pressing a small portion of the dried powder onto the adhesive side of "Scotch" tape, mounted on white card stock. This product gave a distinct color change when exposed for 90 seconds to a mixture of 160 ppm carbon monoxide in air. Further exposure produced a dark, greenish-brown spot.

Samples of this powder appear to be gradually turning green in storage. The level of palladium catalyst has been reduced to 5 μg per gram of test powder; this had little effect on shelf life, but did sharply reduce the masking of the molybdenum color change by palladium black. Addition of 1 mg of ammonium nitrate per gram of powder has been found to preserve the yellow color in storage; however, its effect on the sensitivity of the material has not been determined. It seems probable, however, that the palladium catalyst and ammonium nitrate preservative levels can be balanced to produce a material with both acceptable shelf life and adequate sensitivity.

Additional preliminary experiments are being directed toward production of a suitable opaque support material that would permit observation of color changes <u>in situ</u> through a transparent tape backing. Filter paper pulp, macerated asbestos, and titanium dioxide (added to the slurry) are being examined. A freshly prepared mixture, supported on activated alumina, was successful, but lost both color and sensitivity on overnight standing.

A Teflon jig has been prepared to facilitate preparation of test tape specimens for shelf life testing.

Future Experiments

Shelf life tests will be conducted by applying candidate formulations to "Scotch" tape, covering with release paper, and storing. Some will be stored without further protection; others, in sealed containers.

Samples of commercially available* ammonium-12-molybdophosphate and ammonium-12-molybdosilicate have been ordered for comparison with materials synthesized in the Tech Laboratory.

Respectfully submitted,

[redacted]

W. H. Burrows, Head
Special Projects

WHB/sc

*Research Organic/Inorganic Chemical Corp., Sun Valley, Calif.

ENGINEERING EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

May 31, 1971

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

Attention: Mr. M. C. Stellman

Subject: Fourth Monthly Report, Project A-1308
Contract No. NAS8-26759 - Tracer Sensitive Tapes

Introduction

Work has continued along lines presented in Monthly Report No. 3. Reduction of divalent palladium salts to palladium black and of molybdenum compounds to molybdenum blue in the presence of palladium catalyst have both exhibited sensitivities of the order of 200 ppm; consequently, attention has been concentrated upon building systems incorporating these reactions as tests for strongly reducing tracer gases.

Experimental

(1) Reducing gases

Both carbon monoxide and ethylene have been used with success in producing the above color reactions. Ethylene, although apparently less active than carbon monoxide, is completely non-toxic and can be used without hazard at much higher concentrations than can carbon monoxide. Butadiene might be expected to be more reactive than ethylene, because of the conjugated double bond structure; it is on order and will be included in the next month's experiments.

(2) Reagents

A noticeable decrease in sensitivity to carbon monoxide has been noted in materials prepared from present solutions, leading us to suspect some degree of deterioration. A fresh supply of palladium black is on emergency order to prepare fresh solutions.

The molybdenum compounds examined were ammonium-12-molybdophosphate, ammonium 12-molybdosilicate and an ether extract of a solution of lithium-12-molybdophosphate. The extract is believed to contain the free acid, rather than its salt.

GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

June 30, 1971

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

Attention: Mr. M. C. Stellman

Subject: Fifth Monthly Report, Project A-1308
Contract No. NAS8-26759 - Tracer Sensitive Tapes

Introduction

Experimental effort for this progress period has been concentrated on preparation of test specimens having prolonged shelf life and exhibiting a visible response to 100 parts per million of carbon monoxide in less than five minutes. Additional experiments have consisted of fusing a polyethylene vapor barrier to the test specimen and efforts to prepare a silicomodybdate indicator by treating glass fiber filter material.

Experimental

The ammonium phosphomolybdate specimens used for catalyst level and retarder level experiments were prepared (in the usual way) by immersing glass filter paper in a two percent solution of phosphoric acid in five percent nitric acid. The moistened filter paper was then immersed in a dilute nitric acid solution of ammonium molybdate, allowed to stand for thirty minutes, then washed with copious quantities of distilled water.

Test specimens moistened with several levels of palladium sulfate in dilute sulfuric acid all turned green on drying under an infra-red lamp or on less than a week's standing over indicating silica gel or ammonium nitrate in a desiccator.

Test specimens catalyzed with palladium sulfate and retarded with 0.5 percent solutions of cupric chloride, cupric nitrate, or cupric sulfate all dried to a muddy, greenish brown rather than the desired bright yellow. Specimens retarded with small quantities of ammonium nitrate retained their color when cautiously dried. It is believed that the optimum test material will consist of balanced quantities of palladium sulfate catalyst and ammonium nitrate retarder

in ammonium phosphomolybdate on a glass fiber sheet support. Various levels of catalyst and ammonium nitrate are being explored.

Efforts to prepare a yellow ammonium silico molybdate paper by soaking glass filter paper in strong alkali and subsequent immersion in ammonium molybdate have given only erratic results. Duplicate samples have shown wide variation in color.

It appears that the polyethylene vapor barrier layer between the test strip and its adhesive backing will have to be applied before adding the indicator reagents to the support. Heat sealing the vapor barrier to an ammonium phosphomolybdate "paper" discolors the specimen.

Future Experiments

Work for July will consist of catalyst and retarder experiments and heat sealing experiments with small test specimens. Larger samples will be prepared as soon as the necessary formulations have been established.

Respectfully submitted,

[redacted]

W. H. Burrows, Head
Special Projects

WHB/sc

GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

July 29, 1971

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

Attention: Mr. M. C. Stellman

Subject: Sixth Monthly Report, Project A-1308
Contract No. NAS8-26759 - Tracer Sensitive Tapes

Introduction

Efforts during the current period have been directed toward increasing sensitivity, extending shelf life, and determining the effects of various environmental factors upon the sensitivity and shelf life of the prepared strips.

Experimental

Early efforts were concentrated upon palladium sulfate catalyzed with ammonium phosphomolybdate. Strips prepared by wetting glass paper with this preparation have demonstrated inadequate sensitivity and shelf life; consequently, further work with this material has been abandoned.

By contrast, quite successful results have been obtained with palladium chloride, 0.5% in 10% hydrochloric acid. The glass paper is moistened with this solution and dried in a stream of warm air, producing a light tan colored strip. Upon exposure for approximately one minute to trace quantities of carbon monoxide, the color changes to dark gray. The indicator is responsive to concentrations of carbon monoxide as low as 100 ppm.; its appearance and sensitivity are unchanged over a period of at least two weeks' storage in a closed glass container.

The requirement of non-toxicity of the tracer gas is met by carbon monoxide at 100 ppm, since this concentration is tolerated for 8 hours' exposure without adverse effect. This concentration is also below the flammable limits, even in an oxygen atmosphere.

Palladium chloride test strips have been mounted on "Scotch" brand clear cellophane tape, then convered with release paper. Sensitivity is reduced somewhat from that of the free strips kept in glass containers;

however, the degree of sensitivity loss has not been determined. Further experiments will determine this factor. Also to be explored is the question of the need for the release paper and the barrier film discussed in our Fifth Monthly Report.

Contact with some metals causes darkening of the strips, rendering them useless as indicators. Aluminum and stainless steel produce this effect in 24 hours; copper, in less than 15 minutes. Further contact experiments are underway with other metals, including titanium.

Temperature and relative humidity of the environment during preparation of the strips is a factor in determining sensitivity and shelf life, although the effect is not as yet clearly defined. Optimum performance has been obtained with papers prepared and stored at R.M. 50-55%, with 5 minutes' drying time at 87° C. Experiments are now scheduled for preparations in constant humidity rooms, with various drying times and temperatures. Also included are tests on the incorporation of small concentrations of humectants in the palladium chloride formulation.

Future Experiments

The above paragraphs have outlined the activities for the ensuing period. As soon as the needed factors have been adequately defined, preparation of larger scale test strips will be under way.

Respectfully submitted,

[redacted]

W. H. Burrows, Head
Special Projects

WHB/sc

GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

August 27, 1971

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

Attention: Mr. M. C. Stellman

Subject: Seventh Monthly Report, Project A-1308
Contract No. NAS8-26759 - Tracer Sensitive Tapes

Introduction

Experimental work during the August progress period has been directed toward the preparation of palladium chloride test strips with high sensitivity, prolonged shelf life, and compatibility with the metals commonly used in aerospace hardware.

Experimental

The sensitivity of palladium chloride detector materials is dependent on the presence of moisture. Test strips thoroughly dried in a desiccator at room temperature or in an oven above 100° C were dark in color and showed little or no sensitivity to carbon monoxide. Strips allowed to dry in air of relative humidity 45 to 55 per cent or exposed to a stream of warm air for a brief period darkened on less than a minute's exposure to 100ppm carbon monoxide in air.

The need for moisture in the sensitive layer has required several modifications in the construction of the test tape. A barrier layer permeable to gas but not liquid was required to prevent chemical reaction between the moist test strip and the metal of the structure to be tested. Ordinary filter paper was unsatisfactory because of its hygroscopic character and its reaction with the sensitive layer. Glass fiber paper failed to prevent liquid migration from the tape to the metal substrate. Glass fiber paper moistened with one percent "Siliclad" in water then air dried for twenty-four hours or oven dried at 100° C for ten minutes effectively prevented chemical reaction between the indicator tape and the metal substrate. There was no measurable decrease in sensitivity. The permeability of the barrier layer to gas, however, allowed water vapor to diffuse through the barrier layer and attack the release paper.

After examining several commercially available release papers, a strip of "Mylar" film thinly coated on one side with finely divided polyethylene (a tape used commercially for heat sealing the seams of polyethylene bags) was selected. This material can be stripped from the

face of the laminated test strip before use, has excellent dimensional stability in the presence of moisture, and is impermeable to gases.

Moisture from the palladium chloride indicator strip also attacked the adhesive of the backing tape used to secure the test laminate to the surface being tested for leaks. This attack resulted in darkening of the indicator layer and loss of sensitivity, softening of the pressure sensitive adhesive, and swelling of the backing of the adhesive tape. While substituting a polypropylene backed pressure sensitive tape for the original "Scotch Tape" prevented wrinkling, it did not prevent reaction between the indicator layer and the adhesive itself. It was therefore necessary to place a barrier layer impermeable to vapor between the carbon monoxide-sensitive layer and the adhesive tape. Attempts to heat seal a film of polyethylene to the glass fiber paper resulted in tearing of the paper due to shrinkage of the polymer film on cooling. Heat sealing the commercial Mylar-polyethylene sealing tape to the glass fiber paper before treatment with palladium chloride solution proved to be satisfactory for this application.

An additional experimental obstacle to be overcome was adhesion between the silicone treated barrier layer and the release strip. Experiments are under way to demonstrate that a perforated layer of release tape heat sealed to the silicone treated barrier layer will permit stripping of the outer release layer without separation of the indicator and silicone treated layers.

The construction of the tracer sensitive tape in its current state of development is as follows:

1. A release layer of "Mylar" bag sealing film.
2. A perforated layer of "Mylar" bag sealing film heat sealed to a silicone treated glass paper barrier layer.
3. A palladium chloride treated glass fiber paper sensitive layer heat sealed to a vapor-impermeable Mylar film backing.
4. A layer of pressure sensitive tape.

The widths of the respective layers are so adjusted that the adhesive layer contacts only the release layer, the silicone treated barrier layer, and the vapor impermeable backing of the sensitive layer.

Present and Future Experiments

Several additional adhesive tapes are being examined for resistance to moisture and ease of application to irregular surfaces. All of these adhesive tapes are transparent to permit *in situ* examination of the leak test. A cylinder of test gas (100ppm carbon monoxide in nitrogen calibration mixture) is on order. It is expected that high pressure leak testing can begin early in September.

Respectfully submitted,

[redacted]

W. H. Burrows, Head
Special Projects

WHB/sc

GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

October 5, 1971

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

Attention: Mr. M. C. Stellman

Subject: Eighth Monthly Report, Project A-1308
Contract No. NAS8-26759 - Tracer Sensitive Tapes

Introduction

This month's effort has been directed toward testing the laminated tape described in the previous report, including modifications of the tape suggested by the results of these tests.

Experimental

A testing device has been assembled to permit testing of tape samples at low gas leak rates. The assembly consists of a steel cylinder with cutoff valves at each end, two needle valves for flow rate regulation in series downstream from one of the cutoff valves, and a flat plate assembly with a pinhole orifice downstream from the flow rate control valves. In operation, the cylinder is filled with test gas mixture at 50 psig., and the flow rate through the orifice is adjusted to approximately 10ml/hr. The tape to be tested is then placed over the pinhole orifice and a color change is observed after several exposure periods.

Two test gas mixtures were evaluated. A mixture of 100ppm carbon monoxide (CO concentration "Allowable for an exposure of eight hours") in dry nitrogen gave very slow, almost imperceptible darkening of the test tape. A mixture of 0.1 percent carbon monoxide (CO concentration "Causing unpleasant symptoms, but not dangerous after one hour of exposure") in dry nitrogen turned the test tape from light tan to a dark gray in less than one minute*. This latter mixture was chosen for evaluation of the laminated tape.

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*Matheson Gas Data Book, 4th ed., The Matheson Company, Inc., produced by Herst Litho, Inc., New York, N. Y. 1966.

Slow leakage tests showed that the laminated assembly described in the August report is unsatisfactory for practical use. The volume of the silicone pad layer permits the small quantity of test gas present to diffuse without darkening a spot on the test strip immediately over the test leak. The plastic film barriers also prevented direct, rapid passage of gas through the test strip. Finally, the impermeable adhesive backing also acted as a barrier to passage of the test gas through the tape assembly.

These observations require revision of the construction of the test tape. As no commercial supply of transparent, perforated, pressure sensitive tape has been discovered, it will be necessary to prepare this material in the laboratory. Several thicknesses of polypropylene and nylon monofilament screen cloth have been ordered to substitute for the silicone treated glass paper and plastic layers in the test laminate.

It is expected that the test tape will require storage in a closed jar or sealed plastic envelope to prevent reaction with carbon monoxide in the ambient air. A preliminary test with a 20ml/hr test gas flow and a mesh and perforated adhesive test laminate has shown a perceptible color change in approximately five minutes. This principal experimental problem appears to be that of establishing a low reproducible flow rate for the test gas.

Present and Future Experiments

It is apparent from the preceeding that mechanical aspects of tape construction have a distinct bearing upon the response period and intensity of response of the sensitized strip in the test laminate. Current efforts are directed toward improving response through modifications in tape construction.

It is anticipated that a visit to the George C. Marshall Space Flight Center will be made within the next few weeks, at which time the test strips and testing device will be demonstrated.

Respectfully submitted,

[redacted]

W. H. Burrows, Head
Special Projects

WHB/sc

GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

November 4, 1971

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

Attention: Mr. M. C. Stellman

Subject: Ninth Monthly Report, Project A-1308
Contract No. NAS8-26759 - Tracer Sensitive Tapes

Introduction

This month's effort has been directed toward preparation of a trace sensitive tape giving a rapid response to a low concentration of carbon monoxide in a 10 ml/hr stream of test gas from a pinhole orifice.

Experimental

The test equipment for tape evaluation was described in Progress Report No. 8.

In earlier assemblies having glass fiber filters, the large open pore volume of the screen cloth separating the sensitive element from the metal surface apparently permitted diffusion of the slowly escaping test gas, precluding the concentrated local reaction needed for visible results. These and earlier sensitized strips also suffered from complexity of construction, necessitated by the requirements of isolating the sensitized medium from reducing agents in the filter paper, pressure sensitive tape and metal surface, while still providing access of the test gas to the medium.

A much simpler system has now been developed, consisting of only three components yet giving a visible leak test response to 1000 ppm CO in 2 minutes, or to 100 ppm CO in less than 5 min. The sensitive medium consists of a special screen fraction of silica gel, impregnated with palladium chloride and carefully dried. This medium is pressed into the adhesive side of a perforated transparent pressure sensitive tape just prior to use, and is covered with hardened filter paper to prevent contact with the metal surface.

The silica gel indicator is prepared, as before, by impregnating chromatographic grade silica gel with 0.5 per cent palladium chloride dissolved in 1 per cent hydrochloric acid. The gel is dried until just free flowing and a light tan color develops under infrared heat. The

gel is screened to obtain a fraction less than 100 mesh but greater than 200 mesh. Larger sizes produce a salt-and-pepper upon exposure to CO, while smaller sizes give a diffuse gray spot. Within the selected range, exposure to CO on the test equipment gives a small, sharply contrasting spot, centered over the orifice and visible without magnification against the white background of the filter paper. This medium has not been observed to deteriorate when stored in a tightly closed container.

The tape used is ordinary "Scotch Brand" or equivalent pressure sensitive tape, perforated to prevent back pressure against the leak gas. As yet, no commercial source of perforated tape of this type has been located; hence, perforations were made in the laboratory.

Earlier experiments had used ordinary filter papers to insulate the sensitive medium from the metal surface; however, these quickly reduced the palladium chloride, degrading the medium. In the present experiments, Whatman No. 541 paper, hardened with nitric acid, is used, producing no perceptible reaction with the medium. Apparently, nitric acid removes or oxidizes any reducing agents present in the paper.

As yet, we have found no means for preventing gradual darkening of the indicator gel in contact with a pressure sensitive adhesive. This response, however, requires at least an hour to give visible results, while the test gas produces results in minutes.

Respectfully submitted,

[redacted]

W. H. Burrows, Head
Special Projects

WHB/sc

FINAL TECHNICAL REPORT

PROJECT A-1308

TRACER SENSITIVE TAPES

W. H. BURROWS

AND L. W. ELSTON

Research Contract No. NAS8-26759

November 31, 1971

Prepared for
George C. Marshall Space Flight Center
National Aeronautics and Space Administration

1971

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

ABSTRACT

A leak detection system has been developed, consisting of a tape that can be wrapped around possible leak sites on a system pressurized with air or gaseous nitrogen. Carbon monoxide, at a level of 100 to 1000 parts per million is used as a trace gas in the pressurized system. The sensitive element of the tape is palladium chloride supported on specially prepared silica gel and specially dried. At a CO level of 100 ppm and a leak rate of 10-20 ml/hr, discoloration of the sensitive element is observed in 1.5 to 3 min. The tape and trace gas are compatible with aerospace hardware, safe to handle, and economically reasonable to produce and handle.

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

FINAL TECHNICAL REPORT

PROJECT A-1308

TRACER SENSITIVE TAPES

By

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I. INTRODUCTION

A. Historical review

Detection of minute leaks in pressurized systems poses a difficult task. Soap bubbles, gaseous reactions, etc., that have served as classical leak detectors for many years fail to demonstrate sufficient response within the useful exposure period of the test medium. There is required, instead, a system which can be applied to a suspected leak area, remain in contact for an extended period of time, and show an easily detectable response during that contact period.

As a part of a total project to develop a leak detection system for use on aerospace hardware, this task was directed to the development of a tape that could be wrapped around possible leak sites on a system pressurized with air or gaseous nitrogen containing a suitable reactive trace gas. The tape would contain a sensitive element reactive to the trace gas, such that a color change in the sensitive element would indicate the presence of a leak.

B. Technical requirements

Exhibit "A" of the Request for Proposal stated the technical requirements for the contract work as follows:

1. General description of the work

The work required under this contract consists of literature search and laboratory testing to find a combination of gas(es) and chemicals which would meet the requirements. The end product of the task would be a formal report and a small quantity of material samples that the contractor had determined to be useful.

The literature search and the laboratory testing are expected to progress concurrently with the laboratory evaluating materials suggested by the literature search as they come up.

Approval of the literature search and/or analytical work by the Government is not required before it is evaluated in the laboratory.

2. Material compatibility requirements

The trace gas and the impregnated paper tape shall not react with the materials commonly used in aerospace hardware, including but not restricted to stainless steels, aluminum alloys, copper, brass, polymers used for "O" rings, valve seats, and seals, and lubricants. This inert behavior shall obtain at pressures ranging from 0 PSIA to 4,000 PSI, and at temperatures ranging from -250°F to +250°F.

3. Safety requirements

The gas used as a trace gas in the inert (GN_2 or air) pressurant shall be readily transported, stored, and used with standard pneumatic equipment and practices in common use. The gas shall be nontoxic in all concentrations. Asphyxiation hazard is acceptable. Combustible gases will be acceptable only if the recommended concentration in air is well below the lower limit of combustible ratios.

4. Sensitivity

The sensitivity of the system shall be defined in terms of leak rate and time duration when the sensitized paper is placed over a pinhole simulating a leak. The minimum acceptable sensitivity shall be such that a well defined, easily seen color change shall take place on the paper tape when exposed to a simulated leak of 1×10^{-4} standard cubic centimeters per second (sccs) for one hour. Greater sensitivity is desired if obtainable.

5. Display characteristics

It is desired that the color change will be a direct result of the leaking trace gas; however, a developing technique will be accepted. The display shall be stable at least two hours after removal from the leak.

II. LITERATURE SURVEY

An exhaustive survey of the chemical literature was made to select likely candidate test gases and reagents for the tracer system under investigation. Table 1 is a list of the sources used in this search. This list is an extensive one and would indicate a very time-consuming search; however, the severe limitations placed upon candidate materials in the above technical requirements made the search primarily one of elimination, rather than selection.

It was clear at the outset that, in order to meet the specified requirements of material compatibility and safety, the gas would have to be a low-molecular-weight, not very polar and non-hydrogen bonding species. Its reactivity would have to be fairly high in order to give a visible response within the required limits of concentration and flow rate. On the other hand, its reactivity could not be too high for compatibility with aerospace materials. It was agreed that toxicity was a function of concentration and that use of a sufficiently low concentration to pose no health hazard would comply with the "non-toxic" requirement.

On the basis of these considerations, the following gases were selected for experimental evaluation of their potential as trace gases: oxygen, nitrous oxide, ethylene, 1,3 butadiene, and carbon monoxide. A description of these gases and results obtained in their evaluation are given in the following section.

Table 1

SOURCES INCLUDED IN LITERATURE SURVEY

Analytical abstracts

Bayer, Gasanalyse, Methoden der arbeitspraxis

Beilstein's Handbuch der organischen chemie

Benedetti-Pichler, Identification of materials via physical properties, chemical tests and microscopy

British abstracts

Bulletin signaletique de chemie

Chemical abstracts

Chemisches Zentralblatt

Current abstracts of chemistry and index chemicus

Dictionary of organic compounds

Din, Thermodynamic functions of gases

Elsevier's Encyclopedia of organic chemistry

Feigl, Spot tests in inorganic analysis

Fresenius, Zeitschrift fur analytische chemie

Gmelin's Handbuch der anorganischen chemie

Grignard, Traite de chemie organique

Handbuch der analytischen chemie

Handbook of chemical data (Reinhold, pub)

Handbook of chemistry and physics (CRC, pub)

Hickenbottom, Reactions of organic compounds

Hoppe-Seyler, Handbuch der physiologisch und pathologischchemischen analyse, fur arzte, biologen, und chemiker

Houben-Wehl, Methoden der organischen chemie

International aerospace abstracts

International encyclopedia of physical chemistry and chemical physics

Jacobson, Encyclopedia of chemical reactions

Kirk-Othmer, Encyclopedia of chemical technology

Kolthoff, Treatise on analytical chemistry

Landolt-Bornstein, Physikalisch-chemische tabellen

Lange, Handbook of chemistry

Table 1 (continued)

SOURCES INCLUDED IN LITERATURE SURVEY

Liebig's Annalen der chemie
Mellor, Comprehensive treatise on inorganic and theoretical chemistry
Nihon Kagaku Soran, Complete chemical abstracts of Japan
Nuclear science abstracts
Organic analysis (Interscience)
Organic reaction mechanisms (Interscience)
Organic reactions - Wiley, (pub)
Pascal, Nouveau traite de chemie minerale
Reilly, Physico-chemical methods
Rodd, chemistry of carbon compounds
Ruch, Chemical detection of gaseous pollutants
Scientific and technical aerospace reports
Scott, Standard methods of chemical analysis
Snell, Colorimetric methods of analysis
Snell, Commercial methods of analysis
Snell, Encyclopedia of industrial chemical analysis
Standard methods of chemical analysis (pub-Van Nostrand)
Thorpe's Dictionary of applied chemistry
Timmermann, Physico-chemical constants of pure organic compounds
U. S. Government research and development reports
Weissberger, Technique of organic chemistry
Welcher, Organic analytical reagents
Zeitschrift fur anorganische und allgemeine chemie
Zeitschrift fur physikalische chemie

III. EXPERIMENTAL PROCEDURES AND RESULTS

A. Test gas mixtures (12,13)

The preceeding literature survey revealed only five candidate test gases which were sufficiently active to be detected by a color reaction, and yet were non-flammable, non-toxic, and compatible with the materials used in aerospace hardware over a wide range of temperatures and pressures. Preliminary screening experiments rapidly eliminated all but one of the candidate gases.

1. Oxygen (1-3)

All of the physical and chemical criteria for a test gas were met, but the problem of completely excluding air appeared to be insurmountable in the simple system desired. Among the obstacles to its use were removal of air from the tape after application to the suspected leak, and subsequent release of encapsulated reagents in the order required for a sensitive test. No experimental system for oxygen as trace gas was devised.

2. Nitrous oxide

Preliminary experiments with nitrous oxide indicated that this non-toxic and non-irritating gas could be detected by acidulated starch-iodide test papers, but only after prolonged exposure at a high concentration. No better test was discovered.

3. Unsaturated hydrocarbons (6)

Mixtures of ethylene or 1,3-butadiene with air failed in preliminary experiments to give color changes with indicators at concentrations below their flammable limits.

4. Carbon monoxide (11,12,13)

Carbon monoxide, though ordinarily considered both flammable and highly toxic, could readily be detected at concentrations as low as 100 parts

per million in air. At a concentration of 0.1 percent (1000 ppm) in air the color change was both rapid and easily visible. This latter concentration is well below the flammable limit of carbon monoxide in air and is described as "causing unpleasant symptoms, but not dangerous after one hour of exposure."(13)

B. Indicator systems

Experimental development of indicator devices was restricted to systems for the detection of carbon monoxide. The two types of indicator reactions studied were the reduction of palladium salts to form palladium black, and the palladium catalyzed reduction of yellow salts of molybdenum heteropolyacids to form molydenenum blue. In the latter, the progressive color change from yellow to green to dark blue would be related to the amount of carbon monoxide to which the test tape had been exposed.

1. Test reagents

A major portion of the experimental work was performed with relatively few stock test reagents. The formulation of the principal reagents is described here.

a. Palladium sulfate solution. Chloride free palladium sulfate solutions were prepared by heating palladium black overnight at 600°C and digesting the resulting mixture of metal and oxide under reflux with sulfuric acid for several days. The refluxed mixture, after dilution with distilled water, was filtered through a sintered glass funnel, and the concentrations of sulfate and dissolved palladium in the filtrate were determined. Sufficient distilled water and sulfuric acid were added to give a final concentration of 13 grams of palladium and 330 grams of sulfuric acid per liter. The solution was stored in a polyethylene stoppered Pyrex bottle.

b. Palladium chloride solution (stock). One-half gram of palladium chloride was dissolved in a one-percent solution of hydrochloric acid in distilled water. The solution was stored in a glass stoppered bottle.

c. Ammonium molybdate solution (neutral). Fifty grams of ammonium molybdate were dissolved in 1000 ml distilled water.

d. Ammonium molybdate solution (acid). A cool solution of 100 grams of molybdic oxide in 144 ml of ammonium hydroxide and 271 ml of distilled water was poured slowly, with constant stirring, into a cooled mixture of 489 ml of concentrated nitric acid and 1150 ml of distilled water. The combined solutions were stored in a tightly closed glass bottle for forth-eight hours. Portions of this solution were filtered immediately before use.

e. Phosphoric acid solution. Two ml of 85 percent phosphoric acid and 5 ml concentrated nitric acid were dissolved in 100 ml distilled water.

f. Lithium molybdate in ether. The initial preparation of this reagent was similar to that described above for acid ammonium molybdate except that lithium hydroxide was substituted for ammonia. The prepared salt was extracted from an aqueous solution into diethyl ether.

C. Evaluation of detector systems

1. Testing devices

a. Screening apparatus. The apparatus for initial screening experiments, and later evaluation of candidate systems, consisted of a 500 ml conical beaker whose top was closed by a plastic film retained by a rubber band. A gas tight hypodermic syringe was used to inject the desired amount of carbon monoxide (usually 0.5 ml to give a 1000 ppm concentration). The puncture was closed with "Scotch" tape, and the beaker, containing a few small pieces of

card stock, was shaken vigorously then allowed to stand approximately thirty minutes. Samples were inserted by cautiously lifting one edge of the plastic film and immediately reclosing the container. The samples consisted of strips of the candidate indicator layer or of powdered or granular material pressed into the adhesive side of "Scotch" tape and mounted on white card stock.

b. Leak test assembly. A testing device was assembled to permit testing of tape samples at low gas leak rates. The assembly consists of a steel cylinder with cutoff valves at each end, two needle valves for flow rate regulation in series downstream from one of the cutoff valves, and a flat plate assembly with a pinhole orifice downstream from the flow rate control valves. This assembly, shown in Figure 1, has been demonstrated to George C. Marshall Space Flight Center personnel.

In operation, the cylinder was filled with test gas mixture at 50 psig., and the flow rate through the orifice was adjusted to approximately 10 ml/hr. The tape to be tested was then placed over the pinhole orifice and a color change was observed after several exposure periods.

Two commercially available calibration gas mixtures (The Matheson Company, Morrow, Georgia) were used to evaluate tape samples. A mixture of 100 ppm carbon monoxide (CO concentration "Allowable for an exposure of eight hours"*) in dry nitrogen gave very slow, almost imperceptible darkening of the test tapes. A mixture of 0.1 percent carbon monoxide (CO concentration "Causing unpleasant symptoms, but not dangerous after one hour of exposure"*) in dry nitrogen turned a test tape of palladium chloride on silica gel from light tan to a dark gray in less than one minute. The more concentrated mixture was used for preliminary leak testing. The less concentrated test mixture was

*Matheson Gas Data Book, 4th ed., The Matheson Company, Inc., produced by Herst Litho, Inc., New York, N. Y., 1966.

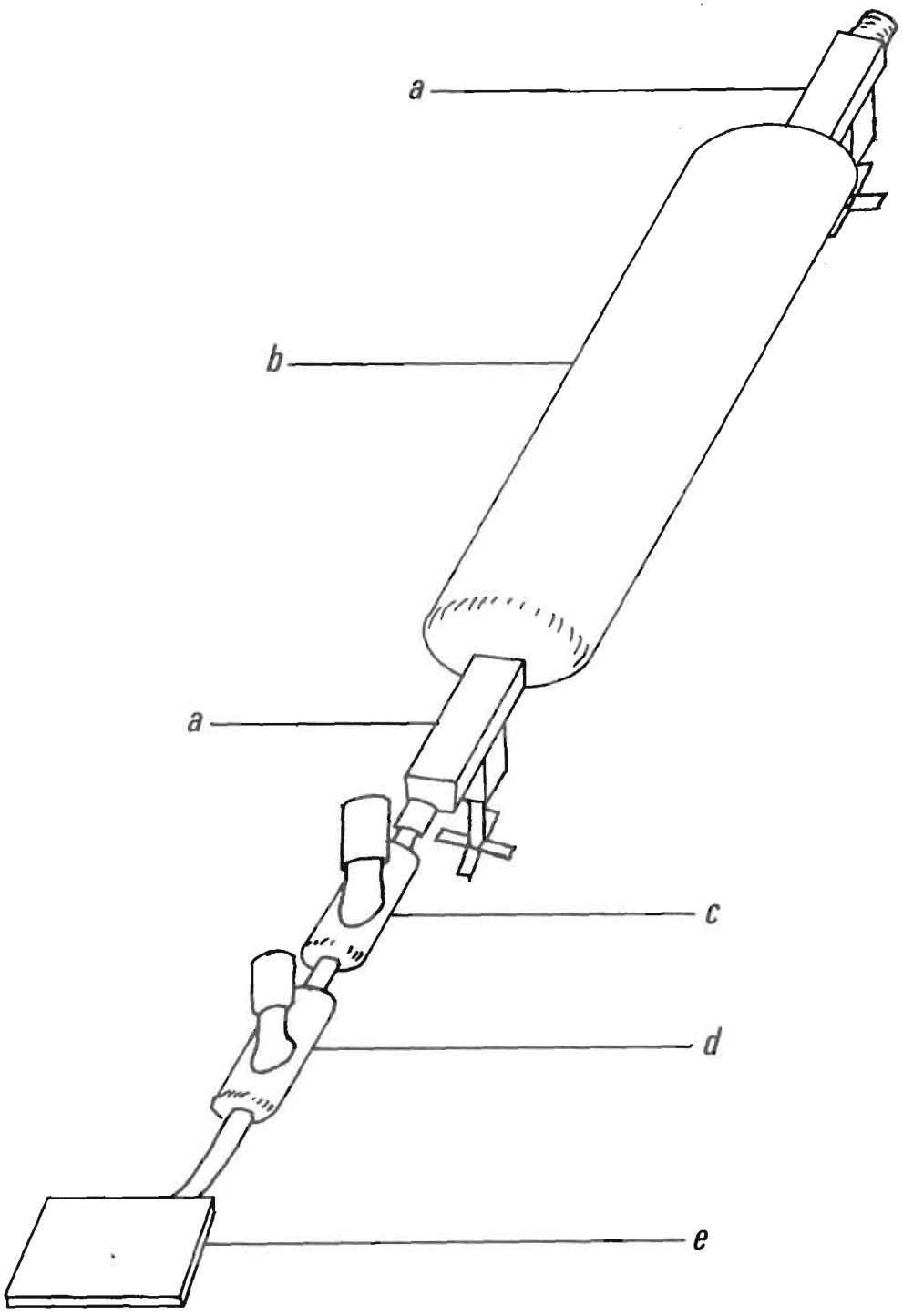

Figure 1. Orifice Test Assembly

a,a - Shut-off valves. b - Gas sampling tube. c - Coarse adjustment. d - Fine adjustment. e - Orifice plate

used for examining tape systems which had appeared highly sensitive with the more concentrated test gas. The time required for a visible response with the dilute (100 ppm CO) mixture in the pinhole leak test was only roughly twice that required with the most concentrated (1000 ppm CO) mixture.

D. Candidate reactions

1. Palladium black systems. (7,8,9)

Support materials used for the palladium salts were: (a) finely divided silicic acid powder, (b) gas chromatography grade silica in several screened particle sizes, (c) Mylar backed TLC (thin layer chromatography) sheets, and (d) silica sheets prepared in the laboratory. Impregnants consisted of: (a) palladium chloride stock solution, (b) palladium chloride stock solution diluted with electronic grade acetone, (c) palladium sulfate solution, and (d) palladium sulfate solution diluted with acetone. The test samples were dried by various means and to various moisture levels before exposure of the test gases.

Although all of the test specimens darkened in mixtures of carbon monoxide or ethylene, the greatest sensitivity was shown initially by palladium sulfate on laboratory prepared silica sheets. Further experiments indicated that the sensitivity of the dried or partially dried samples is closely related to their final moisture content. Samples dried in an electric oven at 100°C or baked under an infrared lamp became dark brown in color and lost most of their sensitivity. Wetting and redrying these overdried samples did not restore their sensitivity. The optimum sensitivity was obtained by drying the impregnated silica gel to a very light tan color, at which point it became free flowing.

Later experiments showed that control of drying could produce a palladium chloride/silica gel impregnate with still greater sensitivity. When dried to optimum sensitivity, palladium chloride impregnated samples, exposed to an atmosphere of 1000 ppm of carbon monoxide in air, darkened visibly in 30 to 45 seconds. The response time for similarly exposed samples impregnated with palladium sulfate was 60 to 90 seconds. Palladium chloride is a commercial chemical; palladium sulfate, a laboratory preparation (see Section B-1).

The appearance of the exposed silica gel sample was strongly affected by particle size. Material retained on an NBS No. 35 sieve darkened in isolated spots to give a "salt and pepper" effect. Samples passing an NBS No. 200 sieve gave a diffuse gray color, which appeared to be relatively slow in developing, probably because of lack of contrast with a white background. Samples prepared on silica passing a No. 35 screen and retained on a No. 100 screen retained some of the "salt and pepper" appearance exhibited by the larger particles. The best visible response was shown by particles passing a No. 100 screen but retained on a No. 200 screen. Particles of this size retained most of the high contrast shown by the large granules and still appeared to be uniformly darkened when viewed without magnification against a white background. The relationship between visibility and particle size held whether the particles were impregnated and dried before or after screening.

Although silica gel impregnated with palladium salts and carefully dried darkens perceptibility on six to 21 day contact with pressure sensitive adhesive, it has a shelf life of at least six months when stored in closed containers. Sufficient moisture is retained to permit redox reactions of the salt with carbon monoxide without free moisture to attack the pressure sensitive tape.

2. Molybdenum blue systems. (3,4,5,7,10)

Laboratory preparation of an indicator gel similar to that used in the National Bureau of Standards Carbon Monoxide Detector System failed to produce the desired bright yellow material. Treatment of dried chromatographic grade silica gel with neutral ammonium molybdate and stock palladium sulfate solution followed by drying in vacuo yielded a white material which gave only the palladium black reaction with carbon monoxide. The shelf life of indicator gel taken from commercially available sealed glass detector tubes was limited to a few hours; hence, attempts to prepare a similar indicator for use on a leak detector tape were abandoned.

A slurry was prepared by mixing 0.5 g of ammonium-12-molybdophosphate in 10 ml acetone, adding sufficient palladium sulfate solution to produce about 250 μg of palladium sulfate per gram of dry product, then mixing well with 5 g of silica gel and air drying. Some tendency for the extremely fine phosphomolybdate powder to separate from the larger silica granules was observed. Test specimens prepared from this product gave a distinct color change when exposed for 90 seconds to 160 ppm carbon monoxide in air. Further exposure produced a dark, greenish-brown spot.

When it was observed that samples of this powder appeared to be turning green in storage, the level of palladium catalyst was reduced to 5 μg per gram of test powder. Little effect on shelf life was observed, but the reduced catalyst level did sharply reduce masking of the molybdenum color change by palladium black.

Four chemical oxidants were examined as retarders to prolong the shelf life of the molybdenum blue test materials. Cupric chloride, cupric sulfate, cupric nitrate, and ammonium nitrate at a level of 1 mg per gram of indicator

powder gave a product which was brown when dry and insensitive to carbon monoxide. The same concentration of ammonium nitrate led to a powder which retained its yellow color for more than six months. Specimens prepared from this retarded powder, however, required more than two hours for a visible response to 1000 ppm carbon monoxide in air. All of the retarders were introduced by pipet into the slurries as dilute aqueous or water-acetone solutions before drying. Reduction of the ammonium nitrate level to 200 μg per gram of powder provided a test powder which was stable in tightly stoppered glass bottles and which gave a color response to 1000 ppm carbon monoxide in air in two to five minutes.

The behavior of commercially available ammonium-12-molybdophosphate and ammonium-12-molybdosilicate (Research Organic/Inorganic Chemical Corporation, Sun Valley, California) was similar to that observed for laboratory prepared ammonium-12-molybdophosphate. The response times for ammonium-12-molybdosilicate, however, were roughly twice those required for the phosphates with identical levels of catalyst, support, and retarder.

E. Support systems

To permit *in situ* observation of leak tests through a transparent pressure sensitive tape backing, some contrasting, opaque support for the colored indicator was required. Filter paper pulp, macerated asbestos, and titanium dioxide were added to the slurry, but proved to be unsuccessful. Mixtures supported on filter paper turned green on drying, probably from traces of reducing agents in the cellulosic material. The powder containing titanium dioxide was white and insensitive. The yellow indicator powder failed to adhere to an asbestos support. A freshly prepared mixture supported on activated alumina was successful but lost both color and sensitivity on overnight standings.

Several test specimens of ammonium-12-molybdophosphate were prepared by supporting a disc of filter paper (Whatman No. 40) on a Buchner funnel, adding a thin slurry of the indicator in water to the funnel, and drawing it to the surface of the paper by means of a water aspirator. These moist discs were catalyzed and retarded by immersion in a Petri dish containing 5 ml of acetone, 0.05 ml (one drop) of a 1:50 dilution of palladium sulfate stock solution, and 0.1 ml of 0.01 percent ammonium nitrate in water. The samples were carefully dried by evaporating the solvent in a stream of warm air. Freshly prepared test specimens gave a color response when exposed to 1000 ppm carbon monoxide in air for less than two minutes. Unexposed specimens cut from the same papers turned green on overnight standing in closed glass containers. Stepwise increases in the amount of ammonium nitrate retarder increased the time required for color response but failed to improve the shelf life.

Similarly prepared samples on glass fiber paper (Reeve Angel No. 934AH) gave similar color response times and improved shelf life. The adherence of the yellow indicator powder to its support, however, was poor.

To avoid the undesirable separation of the indicator from its glass filter support, the ammonium-12-molybdophosphate was prepared <u>in situ</u>. The synthesis was accomplished by immersing glass filter paper in a two percent solution of phosphoric acid in five percent nitric acid. The moistened filter paper was then immersed in acid ammonium molybdate reagent, allowed to stand for thirty minutes, then washed on a Buchner funnel with copious quantities of distilled water.

Test specimens catalyzed with several levels of palladium sulfate in dilute sulfuric acid all turned green on drying under an infra-red lamp or on less than a week's standing over indicating silica gel or ammonium nitrate in a desiccator. Specimens catalyzed with palladium sulfate and retarded with small quantities of ammonium nitrate retained their color when cautiously dried.

Glass filter paper was used as a support for palladium chloride indicator, but the narrow moisture range needed for a sensitive palladium black reaction with carbon monoxide required very careful drying and produced a strip with extremely short-lived sensitivity when exposed to dry air.

F. Laminates

1. Components

a. Pressure sensitive tape. Several transparent pressure sensitive tapes were examined as a means of retaining an indicating reagent layer over a suspected leak. Each of the adhesives contained a reducing agent, which discolored a yellow heteropoly molybdate reagent within a few hours, unless an unacceptably high level of ammonium nitrate retarder was included. The significant differences between the tapes was in dimensional stability and resistance of the adhesive to softening in the presence of moisture. These characteristics are of importance to the shelf life of the tape laminate system, and are summarized in Table 2.

b. Barrier layer. A vapor impermeable barrier layer of plastic film between the adhesive layer and the indicator was required to prevent reduction of the indicator by the adhesive or softening of the adhesive by moisture in the indicator layer. Heat sealing polyethylene film to glass filter paper was unsatisfactory, as shrinkage of the polyethylene film tore the paper. A commercially available polyethylene faced Mylar tape (widely

Table 2

PRESSURE SENSITIVE TAPES

TAPE	DIMENSIONAL STABILITY	MOISTURE RESISTANCE
Scotch Tape No. 810[1]	Poor	Poor
Scotch Tape No. 600[1]	Poor	Poor
Polyken Tape No. 627C[2]	Good	Good
Polyken Tape No. 830[2]	Good	Good
Devoseal No. 1981M[3]	Excellent	Good
Mactac Permanent Adhesive[4]	Excellent	Good
Mystik Tape No. 6400[5]	Excellent	Good

1. Minnesota Mining and Manufacturing Company, St. Paul, Minnesota
2. The Kendall Company, Chicago, Illinois
3. Devon Tape Corporation, Carlstadt, New Jersey
4. Mactac Permanent Adhesive, Stowe, Ohio
5. Borden Chemical, Borden Incorporated, Northfield, Illinois

used for sealing polyethylene bags) was readily heat sealed to glass filter paper without distortion; however, it was necessary to apply the barrier film to the glass paper support before impregnation and drying, as the heat spoiled both molybdenum blue and palladium chloride indicator formulations.

c. Vapor permeable layer. Contact with some metals caused darkening of the sensitized elements, rendering them useless as indicators. Aluminum, stainless steel, and titanium produced this effect in 24 hours; copper in less than 15 minutes. A barrier layer permeable to gas, but not liquid, was required to prevent chemical reaction between the moist indicator strip and the metal structure to be tested.

(1) Filter paper. Ordinary filter paper was unsatisfactory because of its hygroscopic character and its reaction with the sensitive layer.

(2) Glass filter paper. Glass fiber paper failed to prevent liquid migration from the tape to the metal substrate.

(3) Silicone treated glass paper. Glass fiber paper, moistened with one percent "Siliclad" in water, then air dried for twenty-four hours or oven dried at 100°C for ten minutes effectively prevented chemical reaction between the indicator tape and the metal substrate. Screening tests showed no measurable decrease in sensitivity.

(4) Polypropylene monofilament screen cloth. An alternative vapor permeable barrier material, polypropylene monofilament screen cloth in several mesh opening sizes from 105 to 149 microns, was effective in flask testing experiments with palladium chloride on silica gel but permitted too much gas diffusion for pinpoint detection of slow leaks from a small orifice.

(5) Hardened filter paper. A thin filter paper (Whatman No. 541) proved satisfactory when used with palladium chloride supported on silica gel. In testing for leaks from fine orifices the thin paper minimized the lateral gas diffusion inherent in the thicker glass paper or polypropylene screen. Nitric acid washing during the hardening process had apparently eliminated the reducing agents present in ordinary filter paper, and the silica gel support removed the problem of liquid migration.

d. Release layer. After examining several commercially available release papers, a strip of "Mylar" film thinly coated on one side with finely divided polyethylene (a tape used commercially for heat sealing the seams of polyethylene bags) was selected. This material has excellent dimensional stability in the presence of moisture, is impermeable to gases, and can easily be stripped from the face of the laminated test strip.

2. Laminate assemblies

a. Two layer systems. The simplest of the laminate assemblies consisted of an impregnated indicator strip or a band of granular indicator material pressed into the adhesive face of a wider strip of pressure sensitive tape. The indicator layer was degraded by reaction with both the adhesive and the test substrate.

b. Four layer systems. Addition of barrier layers (to prevent unwanted reactions with the indicator layer) and a release layer (to preserve the system during storage) produced a thicker, less flexible laminated tape. The construction of this tracer sensitive tape was as follows:

1. A layer of pressure sensitive tape,
2. A palladium chloride treated, glass fiber paper indicator layer, heat sealed to a vapor impermeable Mylar film backing,
3. A perforated layer of "Mylar" bag sealing film, heat sealed to a silicone treated glass paper barrier layer,
4. A release layer of Mylar bag sealing film.

The widths of the respective layers were so adjusted that the adhesive layer contacted only the release layer, the silicone treated barrier layer, and the vapor impermeable backing of the sensitive layer. An "exploded" schematic diagram of this system is shown in Figure 2.

Experiments with molybdenum blue type indicators in the four layer system failed to produce a tape responding to 1000 ppm carbon monoxide in less than thirty minutes and having a shelf life of more than eight hours; consequently, the experimental program was concentrated on palladium chloride impregnated tapes.

The principal obstacle to the use of moist palladium chloride on glass filter paper was migration of water vapor, which attacked and softened the

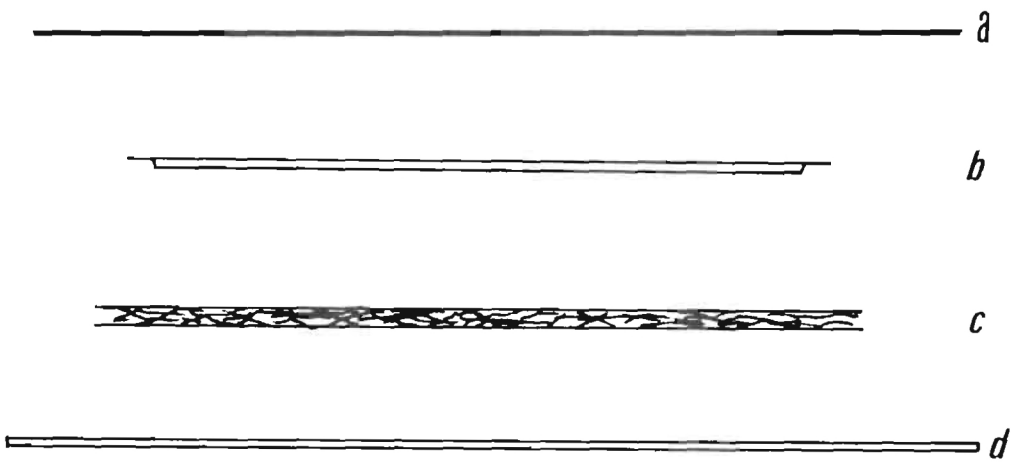

Figure 2. Four Layer Laminate Leak Detection Tape

a. Transparent pressure sensitive adhesive tape. b - Sensitized element.
c. Vapor permeable layer. d - Release layer

adhesive on all of the tapes tested. Distortion of the backing was observed with "Scotch" brand tapes, but not with the other tapes. Failure with all the pressure sensitive tapes occurred as channeling, i.e., a narrow strip opened between the adhesive and the release layer. As moisture escaped through this opening, the indicator became brown and insensitive. This type of failure occurred with all of the four layer tapes in less than 48 hours at room temperature or less than 30 days' storage in a refrigerator at approximately five degrees C.

Although flask tests of this system within four hours after preparation were satisfactory (visible response to 1000 ppm CO in less than two minutes), no response was observed on the leak test device with the high concentration (1000 ppm CO) test gas. Substitution of polypropylene monofilament mesh for the two barrier layers and perforating the pressure sensitive tape backing reduced the flask response time (1000 ppm CO) to approximately one minute, but still no response was observed on the leak test assembly. Applying only a narrow band of pressure sensitive tape to each edge of the assembly to permit free passage of test gas through the indicator layer resulted in rapid drying and loss of sensitivity in the glass paper indicator layer. Substitution of silica gel, impregnated with palladium chloride and carefully dried, for the glass paper indicator gave flask response times of less than one minute but no color change on the leak test assembly.

c. Separate component system. Satisfactory leak test results have been obtained with a system prepared immediately before use. The system consists of 100-200 mesh gas chromatography grade silica gel (Fisher Scientific Company No. S-662) impregnated with palladium chloride solution, cautiously dried under an infra-red lamp, and pressed into the adhesive layer of any of the transparent pressure sensitive tapes listed in Table 2. A layer of hardened filter paper (Whatman No. 541) was used to prevent contact between the indicator

gel and the metal substrate and to provide a contrasting background for the color change. Perforations are needed in the pressure sensitive tape to permit passage of test gas through the tape; these were made manually, as no commercial supplier of transparent, perforated pressure sensitive tape has been found. Screening (flask) tests were conducted with two separately prepared lots of palladium chloride impregnated gel.

Lots A and B were both wetted with palladium chloride solution, and the excess liquid was drained away.

Both samples were dried under a standard 250 watt infra-red lamp (General Electric R-40) at a distance of eight inches. Lot A was dried until the granules just became free flowing and the color was very light tan. The faster Lot B was dried for an additional minute after the powder became free-flowing; its color was slightly darker than that of Lot A. Lots A and B, exposed to 1000 ppm carbon monoxide in air, gave visible response times of 35 and 28 seconds, respectively. Leak test assembly results with tapes prepared from these formulations are summarized in Table 3.

Table 3

LEAK TESTS WITH SEPARATE COMPONENT SYSTEM

Lot No	PPM No	Flow Rate ml/hr	Response Times (minutes) First Visible spot	Medium Gray spot	Dark spot
A	1000	10	2½	5	10
B	1000	10	1-3/4	4	8
A	100	10	6	10	20
B	100	10	4½	7	12

IV. DISCUSSION

An extensive literature survey disclosed only four candidate materials for trace gases: oxygen, nitrous oxide, alkylenes (e.g., ethylene, 1,3-butadiene) and carbon monoxide. Experimental work soon eliminated nitrous oxide and the alkalenes as failing to produce indicator response within the time and concentration requirements. Oxygen, the ideal gas from all other considerations, had to be eliminated because of the impracticability of attempting to eliminate it from the test environment. The developmental program devolved, then, into one of finding the best sensitized element for detecting trace quantities of carbon monoxide and making it into a satisfactory tape for leak detection.

The three reagents most sensitive to carbon monoxide were palladium sulfate, palladium chloride, and ammonium phosphomolybdate, catalyzed with palladium sulfate. Attempts to incorporate these salts into test strips suitable for leak detection on the prescribed scale led to monstrous problems. All are reactive to metals, to plasticizers incorporated in pressure sensitive adhesives, to traces of reducing agents in ordinary filter paper, and to numerous other materials. All require supports, but filter paper, glass paper, silica gel, alumina, asbestos, etc., used for this purpose introduced additional individual problems. An especially serious problem was that of humidity, for it was soon established that each of the sensitized elements required a specific relative humidity range for effective response. Shelf life of the sensitized element could be extended only by enclosure in a container at constant R.H., but under these circumstances adhesives failed, tapes delaminated, paper warped, etc.

Each problem was attacked individually. Various materials were used to insulate sensitive materials from reducing agents, humectants were introduced into the formulations to maintain proper humidity, precipitations in situ and other devices were used to mount the sensitive elements on its supporting medium, etc., but each such innovation gave rise to new problems. To review all of the systems put together and the results obtained with each would require a much more voluminous report than would be justified. Instead, the preceding section presents a summary of the various types of sensitive elements, support media, tapes, etc., utilized, with a full description of the results obtained with each.

The system which was ultimately found to have the sensitivity specified in the technical requirements, together with the material compatibility, safety and other requirements, was one which would solve a number of the problems by eliminating them at their origin. This system utilizes palladium chloride supported on a special grade of silica gel, the system being prepared and dried in a special manner such that the silica gel provides the moisture retention necessary to maintain optimum sensitivity of the palladium chloride. The element thus prepared appears to have infinite shelf life. A special grade of filter paper (Whatman No. 541), which is free of reducing agents that might react with the sensitive element, is used to insulate the sensitive element from the metal surface, while also providing a white background for visibility of the reduced palladium salt. A perforated, transparent pressure-sensitive adhesive tape is used to support the sensitive element over the paper and to attach the system to the surface being tested. The entire system is assembled at the time of its application; hence, shelf life is not a factor.

The system is sensitive to 100ppm of CO in air or nitrogen; at a leak rate of 10-20 ml/hr, discoloration of the sensitive element is observed in 1.5 to 3 min, which is equivalent to the sensitivity requirement of the RFP. Whether the RFP requirement of response in 1 hour to a leak rate of 10^{-4} standard cubic centimeters per second would be met is open to question, as we have not as yet succeeded in producing a reliable leak rate of that magnitude. The limiting factor would be not the sensitivity of the silica gel-palladium chloride element, for that has been proven, but the extent to which lateral diffusion through the filter paper would prevent sufficient penetration of the gas to the element to produce the necessary response. This effect could be reduced by substituting a much thinner separation medium for the filter paper; however, we have not as yet found a substitute which did not introduce additional problems.

It is our judgement, therefore, that the system as herein described and as demonstrated in NASA laboratories meets the technical requirements set forth for this project. In accordance with the terms of the contract, a means for assembling this system is not included in the research, but would be developed in a subsequent project.

V. CONCLUSIONS AND RECOMMENDATIONS

A system has been developed for the detection of leaks of the order of magnitude of 10^{-4} standard cubic centimeters per second of air or nitrogen over a period of 1 hour. The system has been demonstrated for leaks of the order of 10-20 ml/hr, giving positive response in 1.5 to 3.0 minutes. The quantity of gas producing this response is equivalent to that in 10^{-4} cc/sec for 1 hr; however, lateral diffusion in the latter case might reduce the intensity of the response.

The materials required for this detection system are available as items of commerce. The production of the sensitive element from its components is a standard procedure that any properly equipped chemical manufacturer should be able to follow. The system, consisting of sensitive element, perforated pressure sensitive tape and paper backing, is assembled at the time of application.

The gas in the pressure vessel under test will be contaminated with 100 to 1000ppm of carbon monoxide (the upper limit is still well below flammable limits or toxic hazard limits for CO). The carbon monoxide produces the response on the sensitive element of the tape, indicating the presence of a leak.

What the system requires now is a suitable device for the quick assembly of the system and its immediate application to a suspected leak area. The device would contain a hopper for the palladium chloride-silica gel sensitive element, a roll of pressure-sensitive ("Scotch" brand, or equivalent) transparent cellophane tape and a roll of slightly narrower Whatman No. 541 hardened filter paper or its equivalent. The assembler-applicator would

apply a thin coating of the treated silica gel to a strip of the adhesive side of the tape, cover it with the filter paper strip, then apply the assembled system to the leak site.

Accordingly, we recommend that this concept for leak detection be advanced to the state of useful technology through a further project for the design and construction of a suitable assembler-applicator, as described in the foregoing.

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